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MEASUREMENTS OF ULTRASONIC ABSORPTION IN CRYSTALLINE BENZENE

ABRAHAM ROCKMAN

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THESIS

MEASUREMENTS OF ULTRASONIC
ABSORPTION IN CRYSTALLINE
BENZENE

by

Abraham Rockman
Lieutenant Commander,
United States Navy

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Lieutenant Commander, United States Navy

Submitted in partial fulfillment of
the requirements for the degree of

MASTER OF SCIENCE
IN
PHYSICS

United States Naval Postgraduate School
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ABSTRACT

An experimental investigation of the absorption of ultrasonic waves in crystalline benzene was conducted at frequencies of 10 and 30 megacycles per second using a conventional ultrasonic pulse technique. The temperature was varied from -10°C to -105°C.

The absorption coefficient observed at the higher temperature is in agreement with results obtained by Liebermann (4) at 0°C at about the same frequency. The wave velocity observed is somewhat smaller (by about 20%) than that reported by Liebermann.

The wave velocity was observed to decrease linearly with a lowering of temperature. The absorption coefficient was observed to decrease rapidly as the temperature was lowered.

Although the precision of the absorption measurements at 30 megacycles was limited, the results indicate that the absorption increases with frequency raised to about the 1.6 power, a somewhat less rapid rate than frequency squared, which is the dependence reported by Liebermann for the range of 6 to 10 megacycles per second.

The range of temperatures used in this investigation was limited by fracture of the sample. This problem thus limits the drawing of complete conclusions as to the mechanisms responsible for the absorption in crystalline benzene.

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TABLE OF CONTENTS

Section	Title	Page
1.	Introduction	1
2.	Summary of Previous Investigations	3
3.	Experimental Procedures	5
4.	Experimental Results	16
5.	Discussion and Conclusions	21
6.	Bibliography	23

LIST OF ILLUSTRATIONS

Figure		Page
1.	Crystal Growing Apparatus	6
2.	Parallel Facing Apparatus	8
3.	Sample Mounting Apparatus	10
4.	Electronic Circuitry for Making Measurements	13
5.	Graph: Acoustic Velocity vs T (^{o}K)	17
6.	Graph: Absorption Coefficient and Internal Friction vs T (^{o}K)	18
7.	Photographic Record; Exponential Wave Form, Main Pulse and Resultant Echoes	20

1. Introduction.

The phenomenon of sound absorption in solids, especially metals, is not completely understood, but much work has been done in this particular field, (1, 2). However, very little work of this nature has been accomplished with organic compounds in which the molecular binding forces are comparatively weak. Therefore, it is of interest to investigate ultrasonic absorption in organic crystals. L. Liebermann (3, 4) has calculated what he terms a "resonance absorption" in this type of crystal, which involves the weak coupling between the molecular vibrations and the vibrations of the lattice.

The organic compound selected for this and Liebermann's investigations is benzene because of its simple orthorhombic crystalline structure and the fact that its weak binding forces are mainly van der Waals' forces. Results from previous investigations, although sparse, are available for comparison, (3, 4, 5).

Benzene has a melting point of 5.5^{o}C, which allows convenient handling of the solid substance at temperatures not unusually low. A problem of major consequence, however, involves growing a flawless monocrystal of workable proportions and shaping a sample commensurate with making reliable measurements. The benzene crystal is extremely fragile and cannot be subjected to unusual shock without resulting in fractures and other imperfections.

Another area of interest concerns the variation of attenuation of ultrasonic energy with decreasing temperature. Liebermann, in his

work, observed no significant change in absorption down to -58°C although his theory predicts that it should. He also observed that absorption varied approximately as the square of the applied frequency in the range from 6.4 to 10.7 megacycles (4). The unusually high absorption values observed for benzene as compared to other crystalline solids was attributed mainly to "resonance absorption". Liebermann uses this term to describe an absorption process involving coupling of energy between lattice vibrations and molecular vibrations, the frequencies of which may overlap in value. The weak inter-molecular forces give rise to a relatively slow rate of adjustment of energy distribution when the equilibrium is disturbed, such as by a stress wave, and thus, the specific heat is time dependent. Except for the resonance feature of the two vibrating modes (lattice and molecular), the behavior of the acoustic absorption is similar to that of the relaxation phenomena well known in most polyatomic gases and in liquids (6, 7).

It is conceivable, however, that this absorption in benzene may be due primarily to dislocations or perhaps to other mechanisms. Additional information concerning this phenomenon could be attained possibly by evaluating absorption as a function of temperature, using a wider range than did Liebermann. This evaluation is a major objective of this investigation.

2. Summary of Previous Investigations.

Liebermann published the results of his work concerning resonance absorption in crystalline benzene in references 3 and 4. His experimental observations indicate the following values of the absorption coefficient (α) at different frequencies:

α_1 = 0.09 neper/cm at 6.4 mc.

α_2 = 0.24 neper/cm at 10.7 mc.

Based on these two values, he proposed that absorption varied as the square of the frequency.

$$\frac{\alpha_2}{\alpha_1} = 2.7 \; ; \left(\frac{f_2}{f_1}\right)^2 \left(\frac{10.7}{6.4}\right)^2 = 2.8$$

As stated previously, he observed that absorption was practically independent of temperature down to -58°C. The acoustic velocity in this medium, determined by pulse measurements, was 3.1×10^5 cm/sec at 0°C. A correction factor for attenuation due to diffraction was applied to the absorption calculations.

J. H. Dowling and G. R. Schultz (5) studied experimentally ultrasonic absorption in crystalline cyclohexane. Since cyclohexane and benzene are similar in many of their properties, Dowling and Schultz's findings concerning attenuation in cyclohexane are pertinent. The results of their work are tabulated herewith:

α = 0.18 neper/cm at 2.3 mc.

α = 0.25 neper/cm at 3.85 mc.

α = 0.45 neper/cm at 9.3 mc.

All measurements were observed at $0^{\circ}C$ and the acoustic velocity was calculated at 1.52×10^5 cm/sec. In attempting to establish a relationship between absorption and frequency, Dowling and Schultz proposed that absorption possibly varies as the two-thirds power of the applied frequency. Their values for absorption coefficient are of the same order of magnitude as Liebermann's results.

3. Experimental Procedures.

A. Growth of Benzene Crystals.

The benzene samples are grown by crystallization from a melt. Fig. 1 is a photograph of the equipment utilized for the growth process. Reagent grade benzene, available commercially, is placed in a glass container and immersed in a water bath in another glass vessel. Glass is used to provide a visual inspection facility without disrupting the growth process. Both vessels are placed in a drum-type, open-top refrigerator in which the temperature is maintained below $0^{\circ}C$. A thermostatically controlled heat source is applied to the water bath to prevent it from freezing. The water is constantly circulated around the benzene container to insure uniform temperature just above the melting point of the benzene, approximately $6^{\circ}C$. The benzene melt container is covered with an aluminum lid and sealed by a rubber gasket. A copper-tipped cold finger projects through a tight joint in the lid and is extended to the liquid surface. In addition, a copper disk is attached to the cold finger to increase the freezing surface and to permit growth of a larger crystal. After applying vacuum grease to the rim of the melt container, a vacuum is pulled to complete the seal and to "de-gas" the benzene. This procedure also reduces evaporation of the highly volatile benzene and eliminates the ingress of air. The degassing process is highly beneficial in improving the growth of a monocrystal and in increasing the individual crystal size of a polycrystalline formation, if such results. From this frozen mass, monocrystalline portions are shaped and

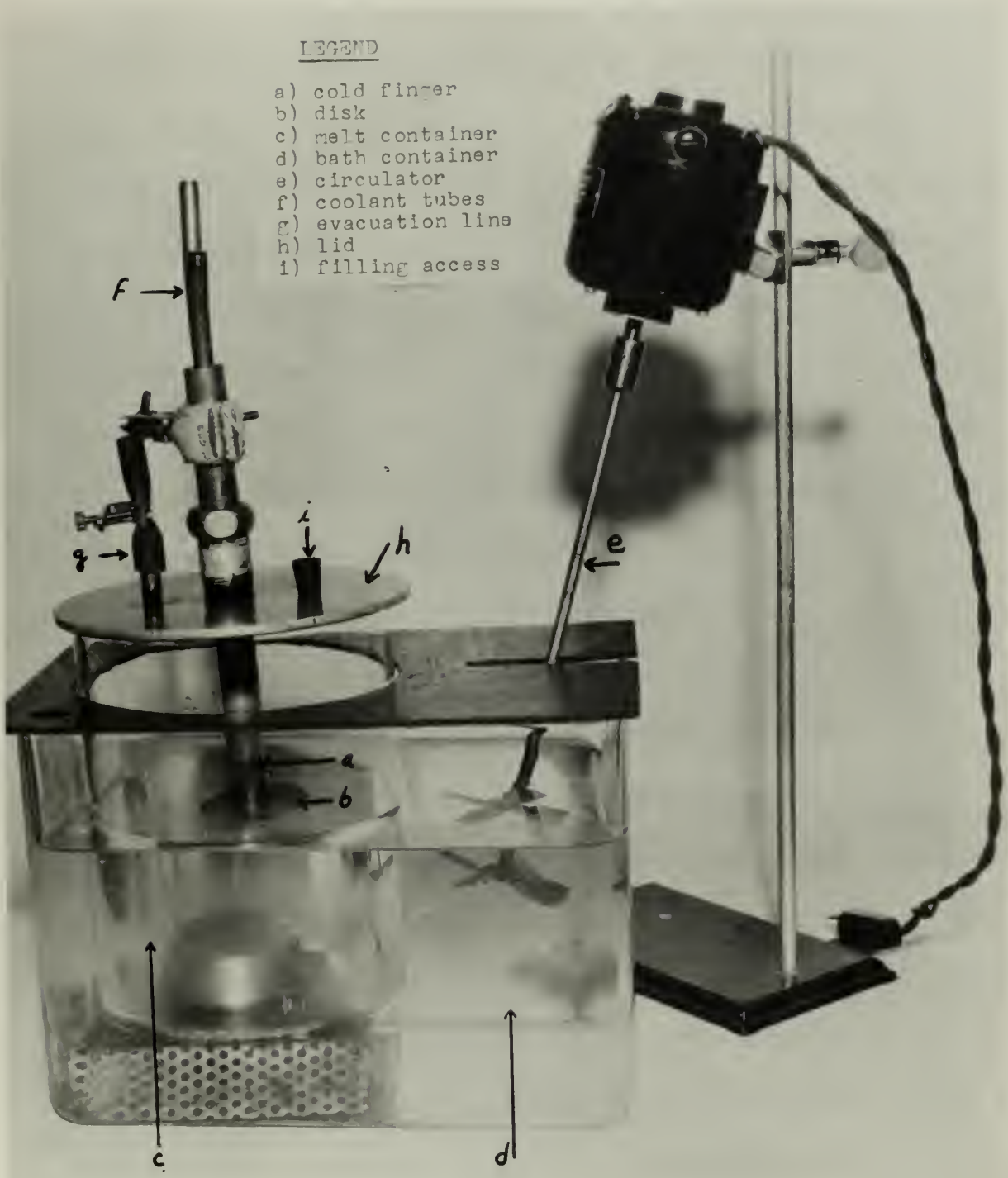

Figure 1. Crystal Growing Apparatus.

used as samples. Upon completion of degassing, cold ethyl alcohol is circulated through the cold finger using a small centrifugal pump to initiate benzene crystallization at the base of the cold finger.

A mirror system is employed to check the progress of crystalline growth. The coolant temperature is lowered periodically as the crystal grows to compensate for the poor thermal conductivity of the benzene crystal. After it reaches approximately seven centimeters in diameter and about five centimeters in length, the growth process ceases for all practical purposes. The cold finger with attached crystal is then transferred to an adjoining refrigerator and the temperature is allowed to equalize before removal of the crystal from the cold finger.

B. Shaping and Preparation of Sample.

The crystalline mass is cut from the cold finger with a small hand-saw. It then is sectioned according to the largest monocrystalline portions available. Insulated gloves are worn whenever handling the crystal to minimize melting. It is desirable to obtain a crystal of about three centimeters in diameter with length dependent on clarity. Polarized light is used to verify absence of fractures and other imperfections. A facing apparatus, shown in Fig. 2, is then employed to produce parallel faces on the crystal by means of melting. This is a prerequisite for accurate measurements. Once parallelism is attained, the small face imperfections caused by refreezing of drippings are eliminated by rubbing on a cold etched-glass surface.

LEGEND

a) sample crystal
b) parallel facers
c) resting stand
d) retractable arms
e) base

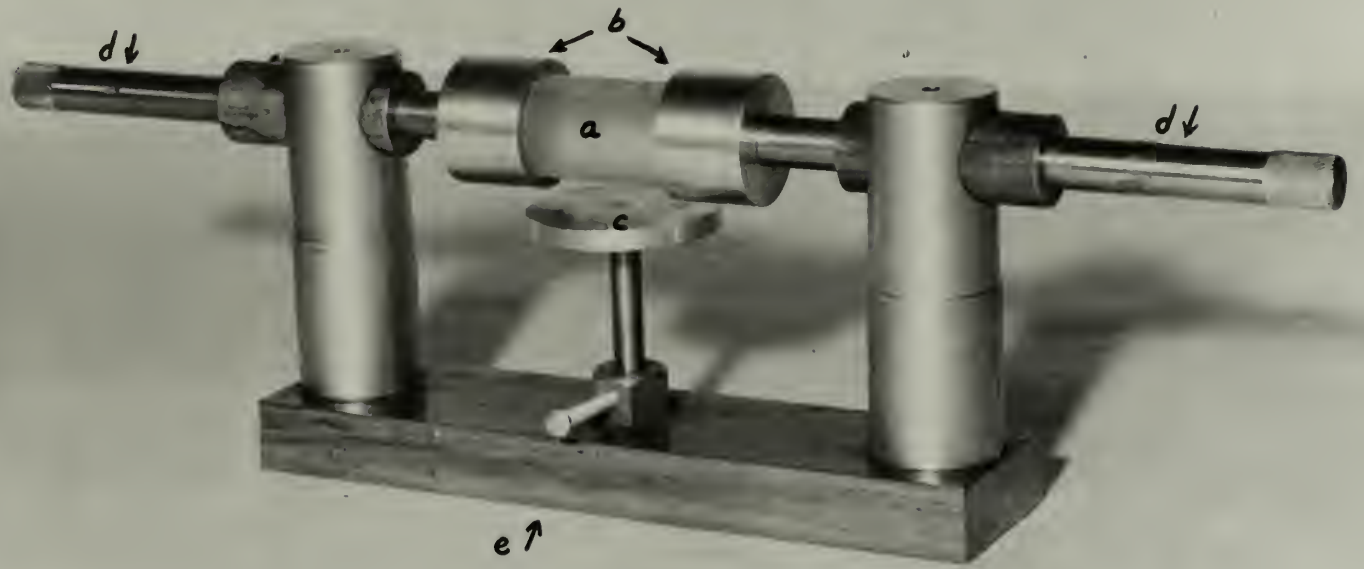

Figure 2. Parallel Facing Apparatus.

A round X-cut quartz wafer of one-half inch diameter and 0.4 millimeter thick is used as a transmitter and receiver of both input signal and resultant echoes. The transducer vibrations must be mechanically coupled to the sample by the use of a very thin seal of joining compound. The fact that benzene is a non-conductor necessitates the use of an intermediate layer of conducting material as an electrode. In these experiments, a one-half mil thick gold plated mylar film is used as this intermediate conducting layer. A tab extension of the film is used for the electrical connection. Glycerine is used as the joining compound between the benzene crystal and mylar film; also between the film and the quartz transducer. Application of pressure to the quartz plate for about 15 minutes squeezes out the excess glycerine and forms extremely thin, secure joints.

The sample is now prepared for mounting.

C. Mounting of Sample and Preparations for Measurements.

The fabricated apparatus as shown in Fig. 3 is used to mount the sample. It provides for a sealed container so that the entire assembly can be suspended in a Dewar flask to facilitate temperature lowering. The container is also needed to reduce the rate of sublimation of the sample and to eliminate the possibility of accidental combustion.

The sample is held by the four spring retainers and the transducer end is pressed against the spring loaded copper disk which serves as the second electrode. If necessary, the sample may also be secured by thread or fine line to the retainers to prevent slippage. The

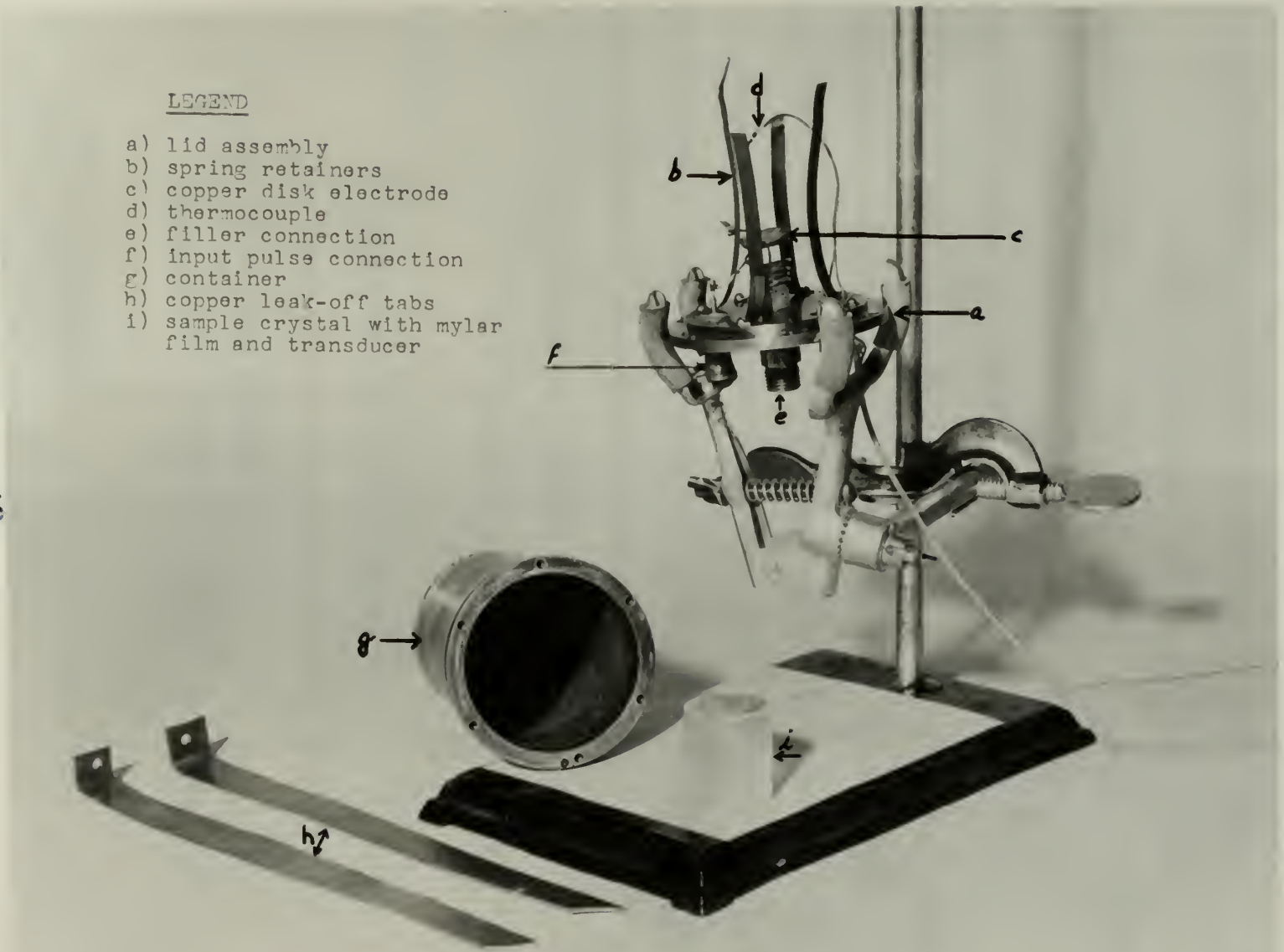

Figure 3. Sample Mounting Apparatus.

mylar film electrode is grounded and the thermocouple connection is placed adjacent to the remote end of the crystal. In this manner measurements are taken at refrigerator temperature, about 263°K.

In order to take readings at lower temperatures, the lid assembly is inverted in the container and sealed. The entire apparatus may then be lowered into a pre-cooled Dewar flask which contains a few inches of liquid air. Two copper tabs are secured to the lid and are used as "leak-offs" by extending their tips into the liquid air. The temperature of the container is lowered gradually by this process and is measured by means of a copper-constantan thermocouple mounted close to the sample. When a desired temperature level is reached, the container is raised slightly in the flask to remove the heat dissipators from the liquid air and the temperature is allowed to equalize.

D. Equipment and Procedure for Making Measurements.

Electronic equipment for making measurements include the following:

a. Pulsed Oscillator, Model PG 650-C

Arenberg Ultrasonic Laboratory, Inc., Boston, Mass.

b. Wide Band Amplifier WA-600

Arenberg Ultrasonic Laboratory, Inc., Boston, Mass.

c. Pulse Generator

AN/USN-27B

d. Oscilloscope, Type 545A

Tektronix, Inc., Portland Oregon

with Plug-in Unit Type 53/54C

Dual Trace Calibrated Preamp

e. Exponential Wave Form Generator

Briefly described herewith is a typical chain of events for making observations. Fig. 4 illustrates schematically the electronics involved. The pulse generator produces a triggering pulse which is delayed slightly and transmitted to the pulsed RF oscillator. A synchronizing pulse is also sent from the pulse generator to the oscilloscope and acts as the sweep synchronizer. The pulsed RF oscillator transmits a trigger to the exponential wave form generator. This is coincident with the outgoing RF pulse from the oscillator to both the transducer and wide band amplifier. There is a 100 ohm load resistor on the outgoing RF pulse line. The exponential wave form generator transmits an exponential wave to the oscilloscope. Using the dual trace plug-in unit with the oscilloscope allows for observation of the main pulse and echoes from the sample, with the exponential wave superimposed.

The pulsed oscillator is now tuned to the transducer resonant frequency which is confirmed by maximizing the echo amplitudes without distorting the echoes. A very careful match of exponential wave to echo peaks is accomplished by manipulating the decay rate of the exponential wave form and slight adjustment of the oscillator frequency. The exponential wave generator has been pre-calibrated and charts have been drawn up corresponding to dial settings. In this manner, once a good match of exponential curve to echo peaks has been attained, the correct decay

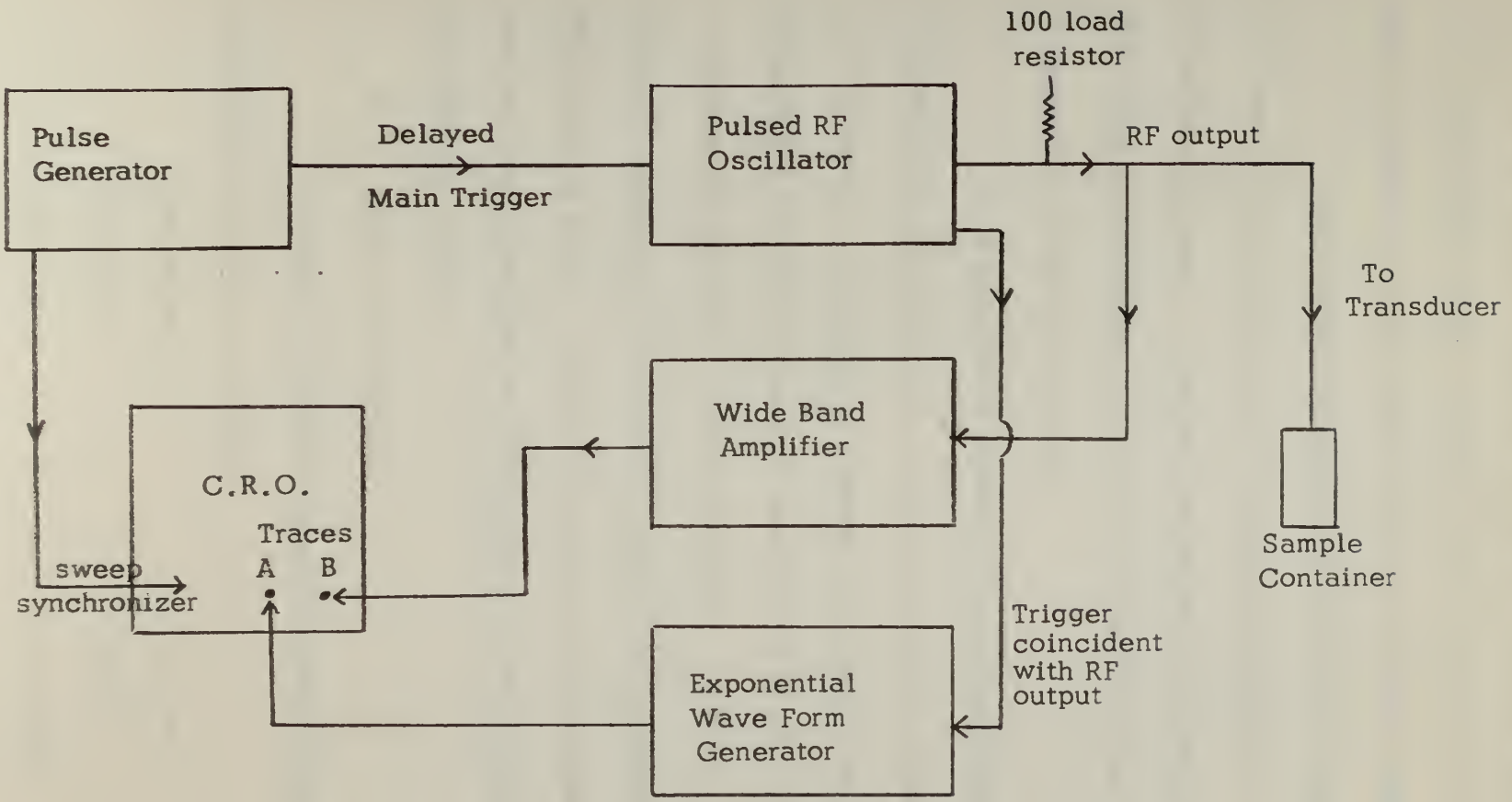

Fig. 4. Electronic Circuitry for Making Measurements

rate in decibels per millisecond is read from the charts. At this point, the thermocouple output voltage is measured using a potentiometer and converted to degrees Kelvin using a conversion chart.

Time delays between main pulse and successive echoes are taken and averaged using the carefully calibrated sweep delay system of the oscilloscope. A precise determination of the tuned frequency is also made by measuring the time interval for 20 cycles on an expanded presentation of one of the echoes.

It is possible to repeat the procedure using odd harmonic frequencies of the transducer to determine how the absorption varies with frequency. In practice, however, this is not easily accomplished because the echoes become very weak and it is most difficult to match an exponential to small, indistinct echoes. At 10 mc, the fundamental frequency of the quartz transducer used here, an adequate signal to noise ratio is found. At the third harmonic of the transducer (30 mc), however, the absorption is much larger and the echo amplitudes are correspondingly smaller.

E. Sample Calculations.

In order to illustrate the calculations made, a typical set of experimental data is presented.

Sample length	1.54 cm
Temperature	$262^{\circ}K$
Decay rate	420 db/ms

Average time delay 12.43 μs

Frequency 10mc

The acoustic velocity in the medium is determined by dividing twice the sample length by the average time delay.

$$\text{Round trip time (time delay)} = \frac{2 \times \text{length}}{\text{velocity}}$$

$$c = \frac{2L}{\text{RT time}} = \frac{(2)\ (1.54)}{12.43 \times 10^{-6}} = 2.48 \times 10^{5} \text{ cm/sec}$$

The absorption coefficient is calculated by dividing the decay rate by the acoustic velocity and applying the conversion factor from decibels to nepers.

$$\alpha = \frac{.420 \times 10^{6} \text{ db/sec}}{.248 \times 10^{6} \text{ cm/sec}} \times \frac{1}{8.68} \quad \frac{\text{neper}}{\text{db}}$$

$$\alpha = 0.195 \text{ neper/cm}$$

The absorption coefficient may be converted to the parameter, reciprocal Q (internal friction) by applying the formula $Q^{-1} = \frac{2\alpha c}{\omega}$ where ω is the angular frequency ($2\pi f$).

$$Q^{-1} = \frac{(2)\ (0.195)\ (.248 \times 10^{6})}{2\pi \times 10^{7}} = 1.54 \times 10^{-3}$$

4. Experimental Results.

Table I is a summary of measurements taken on a benzene crystal, 1.54 cm long, using a frequency of 10 megacycles per second.

TABLE I. Ultrasonic Absorption in Crystalline Benzene

T (°K)	* $c \times 10^{-5}$ (cm/sec)	** α (neper/cm)	*** $Q^{-1} \times 10^{3}$
262	2.48	0.195	1.54
215	2.71	0.104	0.90
198	2.81	0.090	0.81
178	2.91	0.083	0.76
168	2.93	0.075	0.70

* acoustic velocity
** absorption coefficient
*** reciprocal Q (internal friction)

The above data are considered the most reliable taken during this investigation. The match between exponential wave form and echoes from sample was excellent throughout the experimental range. It is apparent that as the temperature decreases, the acoustic velocity in the medium increases. Fig. 5 is a graph of temperature versus velocity and indicates a linear relationship.

At lower temperatures, both attenuation and reciprocal Q decrease. Fig. 6 is a graph of absorption coefficient and internal friction versus temperature; both appear to exhibit an exponential decay with decrease in temperature.

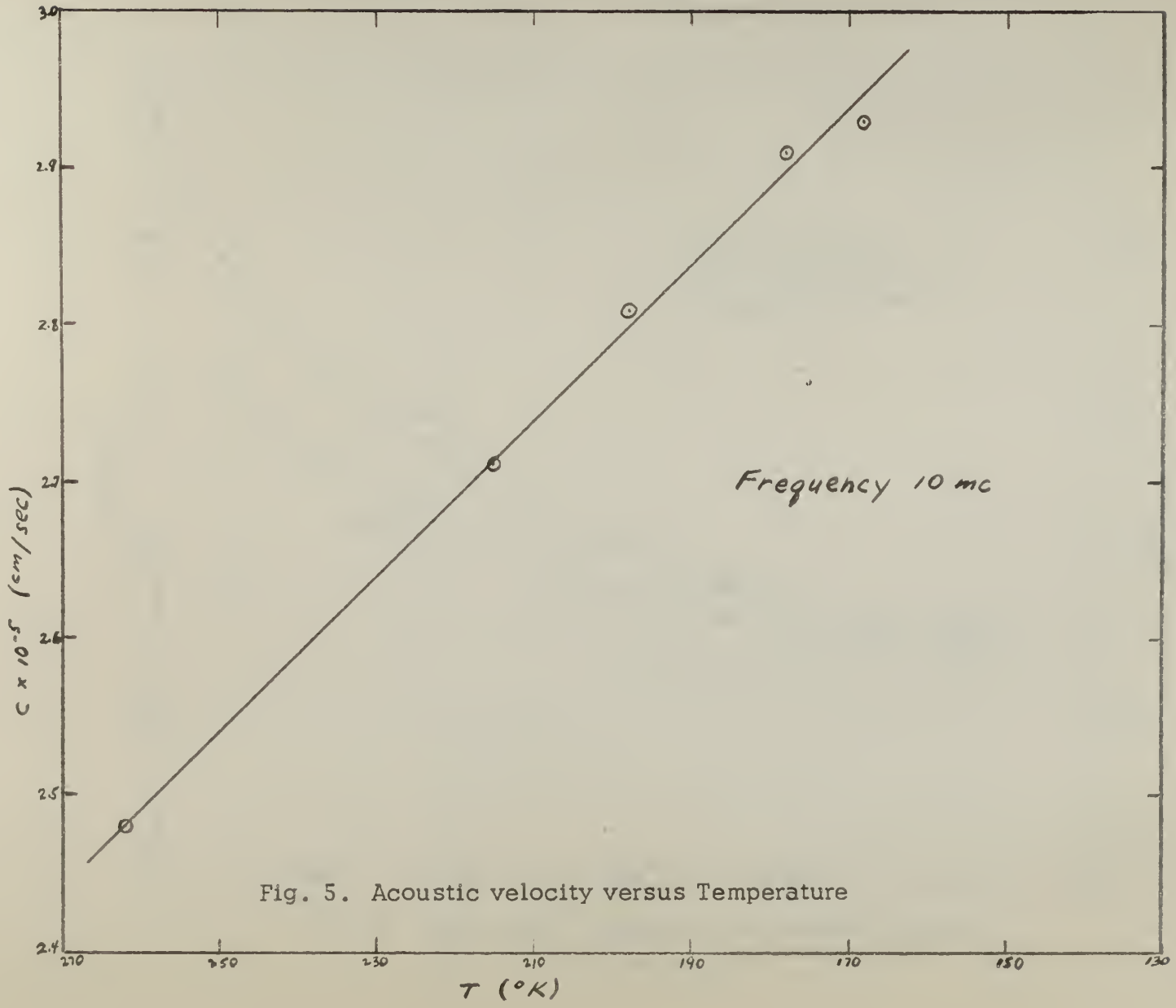

Fig. 5. Acoustic velocity versus Temperature

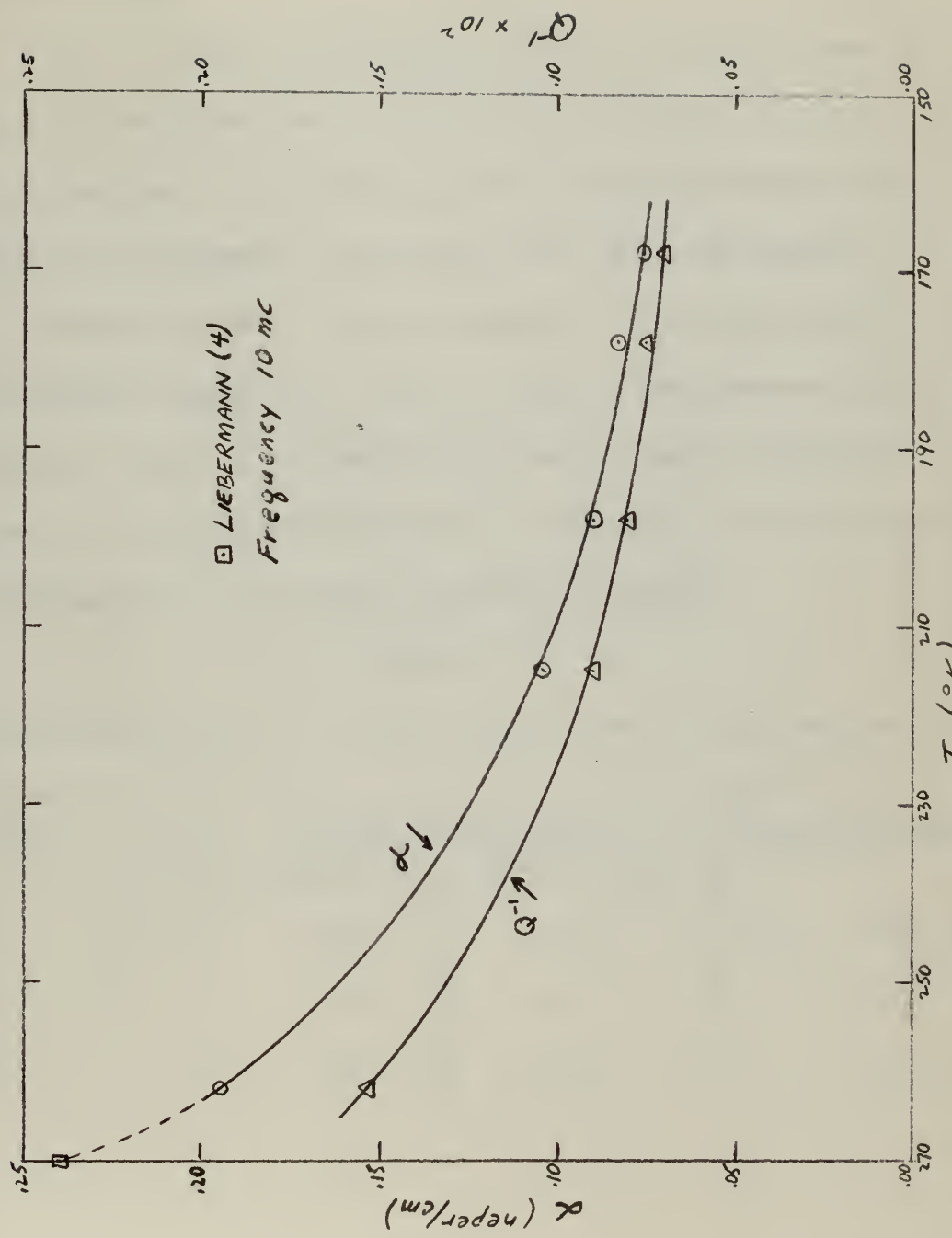

Fig. 6. Absorption Coefficient and Internal Friction vs Temperature

When attempting to lower the temperature below $-105^{\circ}C$, double echoes appeared indicating the sample had failed, probably due to thermal shock.

Fig. 7 is a photographic record of a typical match between an exponential wave form and the RF presentation of main pulse and resultant echoes. One observes that with careful adjustments of exponential and frequency, an extremely close fit can be attained.

The third harmonic frequency (tuned to 30.7 mc) was tried at three different temperatures. Only two echoes were observed at this frequency, indicating a substantial increase in energy absorption. Table II is a summary of the absorption coefficients measured at both frequencies and is presented for comparison purposes.

Table II

Ultrasonic Absorption in Crystalline Benzene at Different Frequencies

T ($^{\circ}K$)	Absorption Coefficient		Ratio of Coefficients
	(at 10 mc)	(at 30.7 mc)	
215	0.104	0.64	6.16
178	0.083	0.50	6.03
168	0.075	0.46	6.13

Figure 7. Photographic Record of Matched Exponential Wave and Echo Peaks.

5. Discussion and Conclusions.

Based on the experimental results, there is a very definite relationship between temperature and absorption. The value for the absorption coefficient appears to follow an exponential decrease within the total range of this investigation, down to $-105^{\circ}C$. There is approximately a two-fold decrease down to about $-70^{\circ}C$ and then the absorption tapers off more slowly. It is suggested that, in future measurements with crystalline benzene, the temperature control be refined so that it can be lowered in small increments over a long period. This should more or less insure the establishment of equilibrium of internal forces. The fracturing of the sample at lower temperatures was a major drawback in this investigation and prevented the attainment of more data at temperatures below $-105^{\circ}C$. One should also limit the input energy to the lowest possible value which is consistent with a favorable signal to noise ratio. Not only will this reduce the probability of crystal fracture but it will also minimize effects of non-linearity of the medium.

The data also indicate that a direct linear relationship exists between acoustic velocity within the medium and decreasing temperature.

Considering the small amount of data available on the absorption-frequency relationship, it can only be suggested that absorption increases rapidly at higher frequency. It appears that the value of the absorption coefficient increases somewhat less than the square of the frequency, perhaps as the frequency raised to the 1.6 power. Additional data will be necessary to establish a more definite relationship between the two, and this is suggested as a future project.

An important factor which was not considered during this investigation was the orientation of the crystal axes while taking measurements. This task became practically impossible with the facing techniques employed. With a more refined procedure, information may be gained on a relationship of absorption and orientation of the crystal.

In addition, it is proposed that repeating the experiment for a shear type wave instead of a compressional wave may prove enlightening. This information can then be combined for a possible determination of elastic constants, using velocity and density to compute Young's modulus and the shear modulus.

Overall, it would be of interest to continue experimentation in this field over wider ranges of temperature and frequency. In fact, this will be necessary in order to determine the details of the mechanisms responsible for the absorption in benzene.

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